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RESEARCH RELATED TO MEASUREMENTS OF ATOMIC SPECIES IN THE EARTH'S UPPER ATMOSPHERE

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A. Introduction and Objective

Precise analysis by rocket- and satellite-borne mass spectrometers of the concentration of atomic oxygen in the earth's upper atmosphere is made difficult by the reactive character of the oxygen atoms themselves. These species can interact with solid surfaces by adsorption, by formation of oxides, and by catalytic production of molecular oxygen. Hence, the oxygen atom concentration as seen by a mass spectrometer may be substantially different from its real value in the environment because of atom removal on the various surfaces of the instrument. The objective of this project is to elucidate the kinetics and mechanisms of interaction of oxygen atoms with solid surfaces of engineering interest under conditions similar to those encountered in the upper atmosphere. Such information will contribute to the quantitative interpretation of atomic-oxygen composition data reported by mass spectrometers in flight.

Our experimental approach employs a reaction vessel in which the total gas pressure and the entering flux of oxygen atoms are held constant. The rate of interaction of oxygen atoms with a metal surface is evaluated by observing the diminution in atom flux at the outlet of the vessel when a specimen of the material of interest is inserted into the reactor. The apparatus was described in Quarterly Status Report No. 4 (June 1, 1968) and the analytical basis of the experiment was discussed in Quarterly Status Report No. 5 (September 1, 1968).

B. Experiments

1. Apparatus

The reactor employed in the current experiments is a Pyrex cylinder with an inside diameter of 2.2 cm and a length of 12 cm (Fig. 1). Atoms are generated by thermal dissociation of molecular oxygen on an electrically heated tungsten ribbon in a water-cooled chamber at the lower end of the reactor. The reactor inlet is a 0.2-cm-radius aperture in a glass plate situated in close proximity to the tungsten ribbon. A radiation shield of tungsten foil between the hot ribbon and the aperture

plate prevents overheating of the glass parts of the reactor in this vicinity. The reactor outlet is a 0.55-cm-radius aperture in a glass plate which leads directly to a large chamber pumped to low pressure by a titanium sublimation pump and an ion-getter pump. This chamber contains a quadrupole mass spectrometer placed so that its ion source is immediately adjacent to the reactor exit aperture. The pressure in the system can be measured by ion gages near the oxygen inlet and on the analyzer chamber. In the current experiments, the specimen is a ribbon of 0.002 inch gold foil, 20.4 cm long by 0.6 cm wide. The ribbon was suspended from its ends on electrical feed-throughs at the upper end of the reactor.

2. Mass Spectrometer Calibration

The geometry of the apparatus is such that the mass spectrometer detects the effective flux of species emerging from the exit aperture of the reactor. For calibration, the total mass flow of gas Q through the reactor was computed from measured pressure differences between the inlet and analyzer ion gages and the calculated overall conductance of the apparatus between these two pressure-measuring points. In the range $10^{-5} < Q < 10^{-3}$ torr-liter/sec, the mass spectrometer signal was found to be proportional to Q with a proportionality constant of 2.13×10^{2} torr-liter/sec/amp. The observed values of Q, together with the values of conductance F calculated from the apparatus geometry, enabled us to compute the steady state pressure P in any part of the system from the basic Knudsen flow equation:

$$Q = F(P_2 - P_1)$$

3. Measurements

a. Recombination Efficiency of Gold

On the basis of our earlier results,[1] greater than 99% of the oxygen atoms entering the reactor, n_1^*, survive and leave through the exit aperture. This is in conformity with the reported[2] value of approximately 10^{-4} for the recombination coefficient of Pyrex glass for

oxygen atoms. Such a small rate of loss of atoms in the empty reactor enables us to easily measure the change in rate of removal of atoms when a gold specimen is inserted into the reactor. The surviving atom flux, n_1, for this situation is observed under identical flow conditions. The recombination coefficient γ of the gold is then obtained from the relation[1]

$$\gamma = [(n_1^*/n_1) - 1]/\sigma \qquad (1)$$

The effective collision number of the specimen σ is the ratio of the specimen surface area A_s to the cross sectional area of the exit aperture A_e. This ratio is 26 for the gold specimen.

b. Rate of Sorption of Oxygen Atoms on Gold

Oxygen sorbed on the gold ribbon during exposure to gaseous atomic oxygen. Following this exposure, the ribbon was heated to 600°C by passing an electric current through it, and molecular oxygen was rapidly desorbed. This was manifested as a pressure pulse detected by the mass spectrometer locked on AMU 32. The total mass of oxygen desorbed from the ribbon during the heating period was evaluated by integrating the pressure rise with respect to time. In several experiments oxygen was desorbed at lower ribbon temperatures, 300° and 500°C, yet the total mass of oxygen desorbed from the saturated surface was constant. The time required to desorb all the oxygen, of course, was longer at lower flashing temperatures.

By observing the total mass of oxygen desorbed as a function of the time of exposure of the specimen at 25°C to the atomic oxygen, the rate of coverage of the gold by sorbed oxygen could be measured. The ratio of rate of coverage to incident collision rate of oxygen atoms on the gold is termed the sticking coefficient, S.

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1. Quarterly Status Report No. 5, September 1, 1968.
2. H. Wise and B. J. Wood, Advances in Atomic and Molecular Physics, 3, New York, Academic Press 1967, p. 322.

c. Rate of Desorption of Sorbed Oxygen at 25°C

Surface sorbed oxygen on gold was observed to desorb spontaneously at 25°C. We measured the rate of this desorption by the following procedure. The specimen was first exposed to atomic oxygen for a sufficient length of time to insure saturation coverage of sorbed oxygen. The oxygen atom source was then cooled to a temperature at which thermal dissociation of oxygen was negligible even though the total oxygen pressure in the system was not changed significantly. After a period of time the gold ribbon was flash heated and the quantity of oxygen desorbed was determined. This procedure was repeated for a number of different dwell periods up to 30 minutes in duration.

d. The Behavior of Impurity Carbon Monoxide

Carbon monoxide was the major residual impurity in our vacuum system. This gas has been reported[3] to chemisorb strongly on gold; hence we felt it important to evaluate the rate of sorption and the degree of coverage exhibited by carbon monoxide under the conditions of our experiments. The rate of coverage and sticking coefficient in the absence of atomic oxygen were determined in a manner identical to that employed for oxygen atoms.

4. Results

a. Recombination Efficiency of Gold

Data obtained in experiments with and without the gold specimen in the reactor lead to a value of $\gamma = 0.062$ for the recombination coefficient of atomic oxygen on gold at 25°C. The tungsten ribbon was maintained at 1850°C during these experiments, and the atom flux was evaluated from the mass spectrometer signal in terms of the ratio AMU 16/ AMU 32.[4]

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3. B. M. W. Trapnell, Proc. Roy. Soc., A218, 566, (1953).

4. Observed values of AMU 16 were corrected for contributions from O_2, CO, and H_2O due to cracking in the mass spectrometer ion source.

The value of the recombination coefficient was also determined independently in another set of experiments in which the reference flux of atoms, n_1^*, was determined while the gold specimen was maintained at 600°C. At this temperature the coverage of the gold surface by sorbed oxygen appeared to be negligible, hence recombination on the gold could not occur. When the gold was cooled to room temperature and re-equilibrated with its environment, a monolayer of sorbed oxygen was re-established and the specimen became again an active recombination catalyst. The surviving flux of atoms n_1 at the reactor outlet was diminished proportionately. Based on the data from these experiments, $\gamma = 0.049$.

b. Rate of Sorption of Oxygen Atoms on Gold

The mass of oxygen sorbed as a function of time of exposure to an atmosphere containing atomic oxygen at $P = 10^{-7}$ torr is shown in Fig. 2. The sticking coefficient for atomic oxygen on gold, derived from this data, is given as a function of surface coverage in Fig. 3.

c. Rate of Desorption of Sorbed Oxygen at 25°C

The mass of sorbed oxygen remaining on the surface of the gold as a function of dwell time in molecular oxygen at $P = 2 \times 10^{-6}$ torr is shown in Fig. 4. All points on this curve are relative to saturation coverage at time $t = 0$.

d. The Behavior of Carbon Monoxide

The sticking coefficient of carbon monoxide as a function of coverage at two impurity levels and total pressures is shown in Fig. 5.

C. Discussion

The values of oxygen atom recombination coefficient obtained for gold in our apparatus by two distinct and different experiments agree within 25%. The precision with which γ can be determined depends, in one case, on the reproducibility of both the mass flow rate of oxygen through the system and the temperature of the tungsten ribbon before and after the system has been opened to the atmosphere to install the

gold specimen, then re-evacuated and baked out. Two ion gage measurements and an optical pyrometer reading are required to assess these parameters. The precision with which the AMU 16/AMU 32 ratio can be determined with the mass spectrometer must be considered in both experiments. Consequently it seems justifiable to state the value of the recombination coefficient to one significant figure: $\gamma = 0.06$. This is in agreement with the value reported earlier[1] based on our first experiments.

Both reported values of γ were obtained after the gold specimen had been exposed to the atmosphere containing atomic oxygen for at least 15 minutes. Under the conditions of our experiments, the gold specimen became saturated with sorbed oxygen after an exposure of about 5 minutes (Fig. 2); hence the observed recombination rates represent steady-state values for an oxygen-saturated gold surface at 25°C.

Although oxygen from the gaseous atomic state is sorbed readily on gold (Fig. 3), we could detect no sorption of oxygen from the molecular state in our experiments. However, in other experiments in our laboratory,[5] less than 0.01 monolayer of oxygen was found to sorb from an atmosphere of molecular oxygen at $P = 10^{-7}$ torr when the temperature of the gold was raised to 300°C. These data, together with the ease with which sorbed oxygen desorbs at low temperatures (Fig. 4), suggest that gold sorbs oxygen endothermically and possesses a modest activation energy for desorption. Based on Redhead's rule of thumb[6] relating the temperature T at which desorption becomes significant to the activation energy for desorption E_d, we conclude that E_d for oxygen on gold is less than 25 kcal/mole.

Our data indicate that at saturation the population density of oxygen atoms on the gold surface is 2.0×10^{15} atoms/cm^2 (Figs. 2 and 3). If we assume, as is usually done, that the density of surface adsorption sites on a metal is 1×10^{15} cm^{-2}, this leads us to conclude that the gold used in our experiments possessed a roughness factor of 2. However, the saturation surface coverage which we report is based

5. N. Endow, to be published.
6. P. A. Redhead, J. P. Hobson, and E. V. Kornelsen, Advan. Electronics Electron Phys., 17, 340 (1962).

on our calibration of the mass spectrometer against the oxygen pressure drop measured with ion gages, and conductance calculations based on the dimensions and geometry of the apparatus. Experimental errors here could lead to uniformly high values of coverage. Compact metals are generally considered to possess a roughness factor of less than 2, but the same metals in the form of evaporated films may exhibit roughness factors as high as 10.

The sticking coefficient of carbon monoxide on gold (Fig. 5) is more than 2 orders of magnitude less than that for atomic oxygen (Fig. 3). The saturation coverage observed in our experiments is about one-sixth that of oxygen, but it exhibits a dependence on the carbon monoxide pressure. A comparison of the room-temperature desorption rate of oxygen (Fig. 4) and the sorption rate of carbon monoxide, shown by the broken curve in Fig. 4, indicates that displacement of sorbed oxygen by carbon monoxide is not involved in the oxygen desorption mechanism.

D. Practical Conclusions

The parameters we have evaluated in our laboratory experiments will be of value in interpreting the oxygen atom concentration data reported by the OGO-F satellite mass spectrometer with the gold-plated sampling antechamber.

1. The time required to saturate the gold surface of the antechamber by atomic oxygen can be computed from the sticking coefficient. The variation of sticking coefficient with coverage is so small that for practical purposes one can consider it constant up to full surface coverage.

2. For data obtained in an atmospheric region in which the antechamber surface can be considered to be saturated with sorbed oxygen, the value of AMU 16 reported by the instrument should be corrected for atom loss by recombination in the antechamber. Based on the dimensions supplied to us on an engineering sketch of this part of the mass spectrometer, the average collision number σ of the antechamber is 81. Using this value for σ and the recombination coefficient $\gamma = 0.06$ in Eq. 1, the fraction of sampled atoms that enter the ion source of the mass spectrometer, n_1/n_1^*, is 0.17.

3. If the satellite, because of the eccentricity of its orbit, spends periods of many minutes in regions of low oxygen atom density, the effect of de-saturation of the antechamber surfaces must be taken into account. The fraction of the surface populated with oxygen atoms will exhibit a dynamic dependence on the rates of sorption (sticking coefficient) and desorption. The variation might be quite complex, but, in principle, should be tractable if the sorption/desorption rates derived from our experiments are used. If a means could be provided to keep the antechamber walls at a high temperature, oxygen atom sorption and recombination would be negligibly small, and these corrections would be obviated.

Future Plans

Our immediate plans are to investigate the oxygen-atom interaction characteristics of other metals. Silver and titanium are of special interest at present, because both metals have been employed in the inlet and ion source regions of flight mass spectometers.

Personnel

Personnel who have participated in this program during the past quarter include Jan W. Van Gastel, Henry Wise, and Bernard J. Wood.

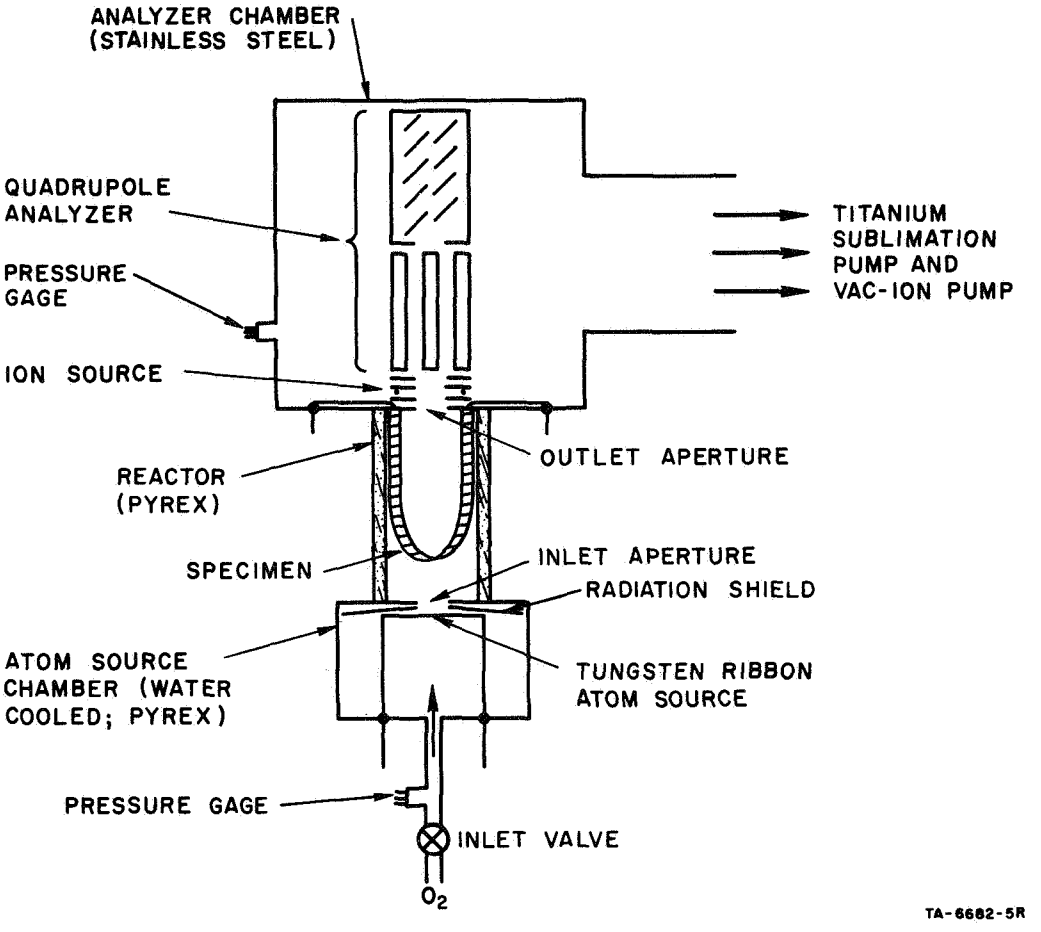

FIG. 1 SCHEMATIC DIAGRAM OF APPARATUS

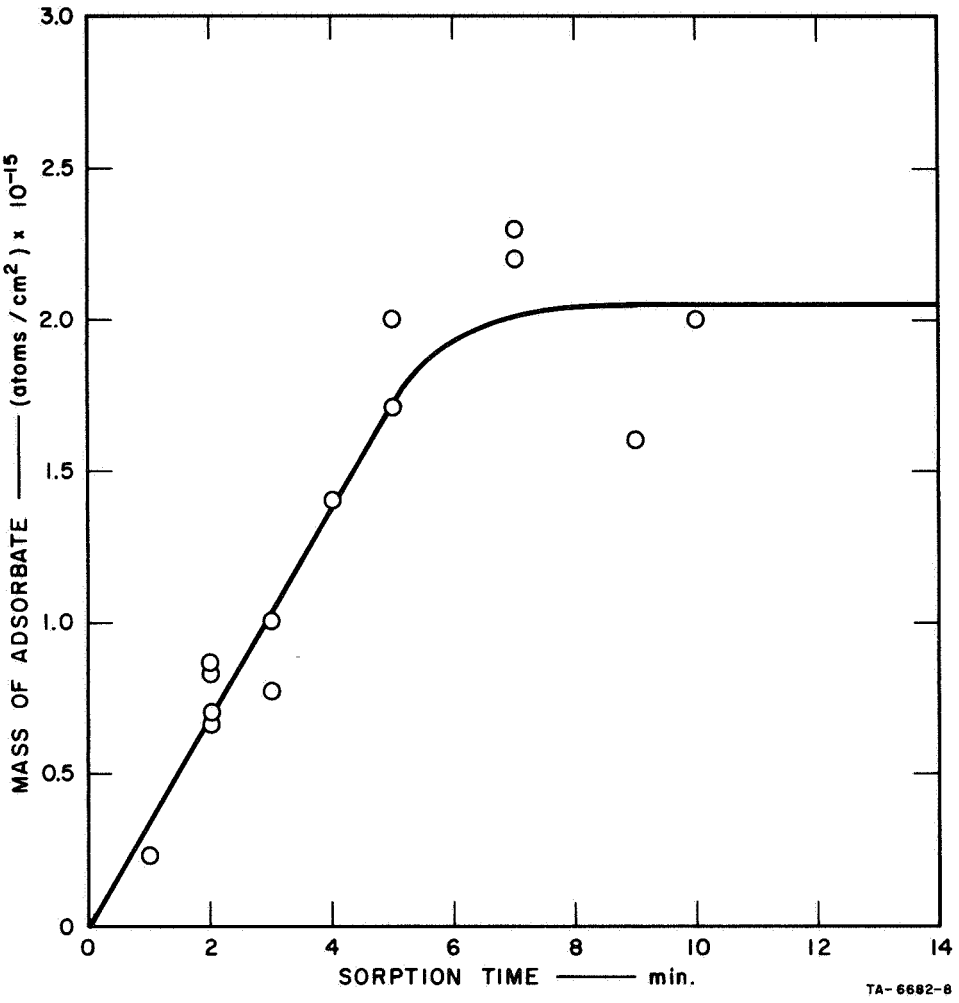

FIG. 2 MASS OF OXYGEN ATOMS SORBED ON GOLD AS A FUNCTION OF EXPOSURE TIME. P_O = 1 x 10^{-7} torr; P_{O_2} = 3 x 10^{-6} torr; T_{gold} = 25° C.

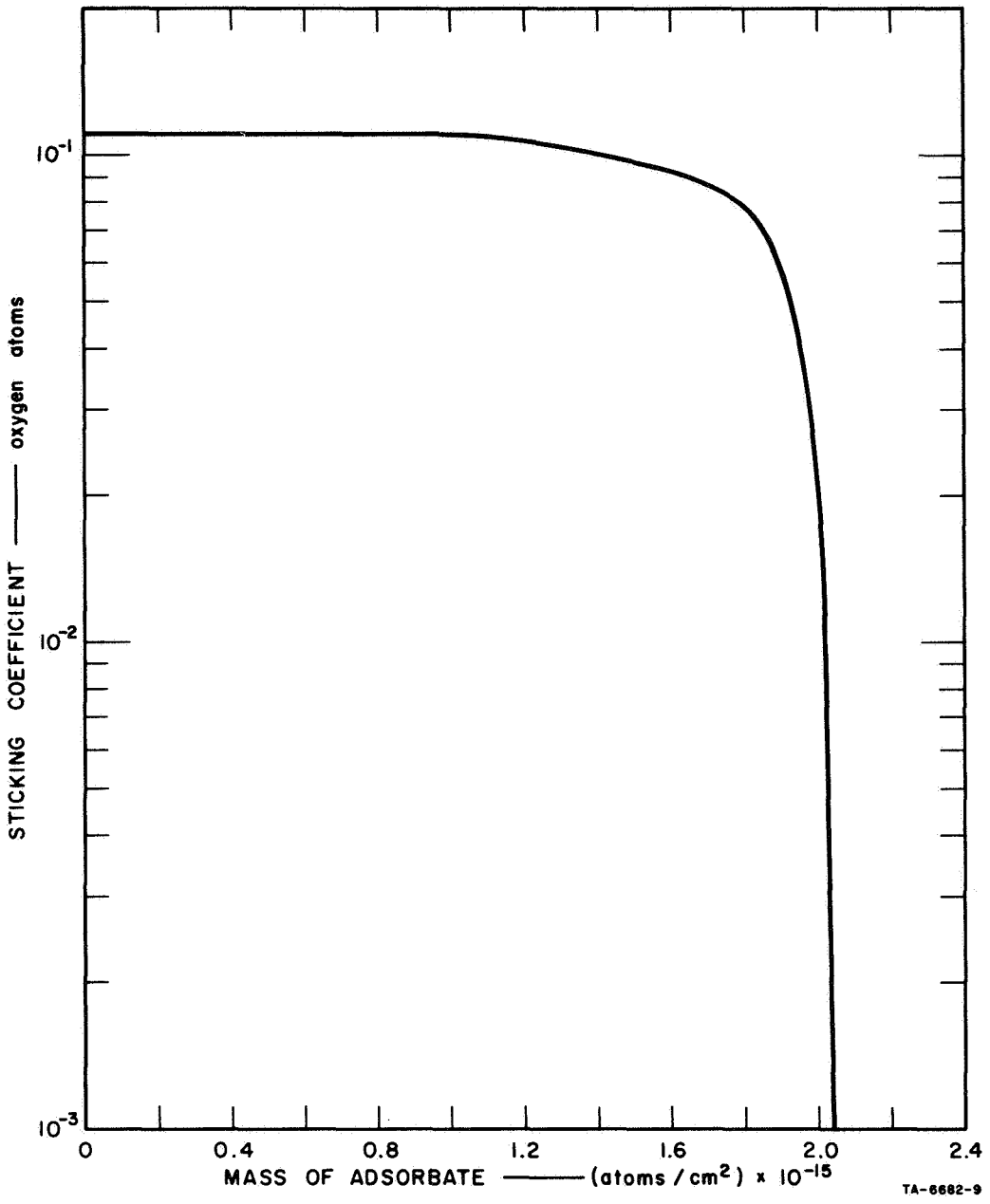

FIG. 3 STICKING COEFFICIENT OF OXYGEN ATOMS ON GOLD AS A FUNCTION OF OXYGEN COVERAGE. Curve derived from data in Fig. 2.

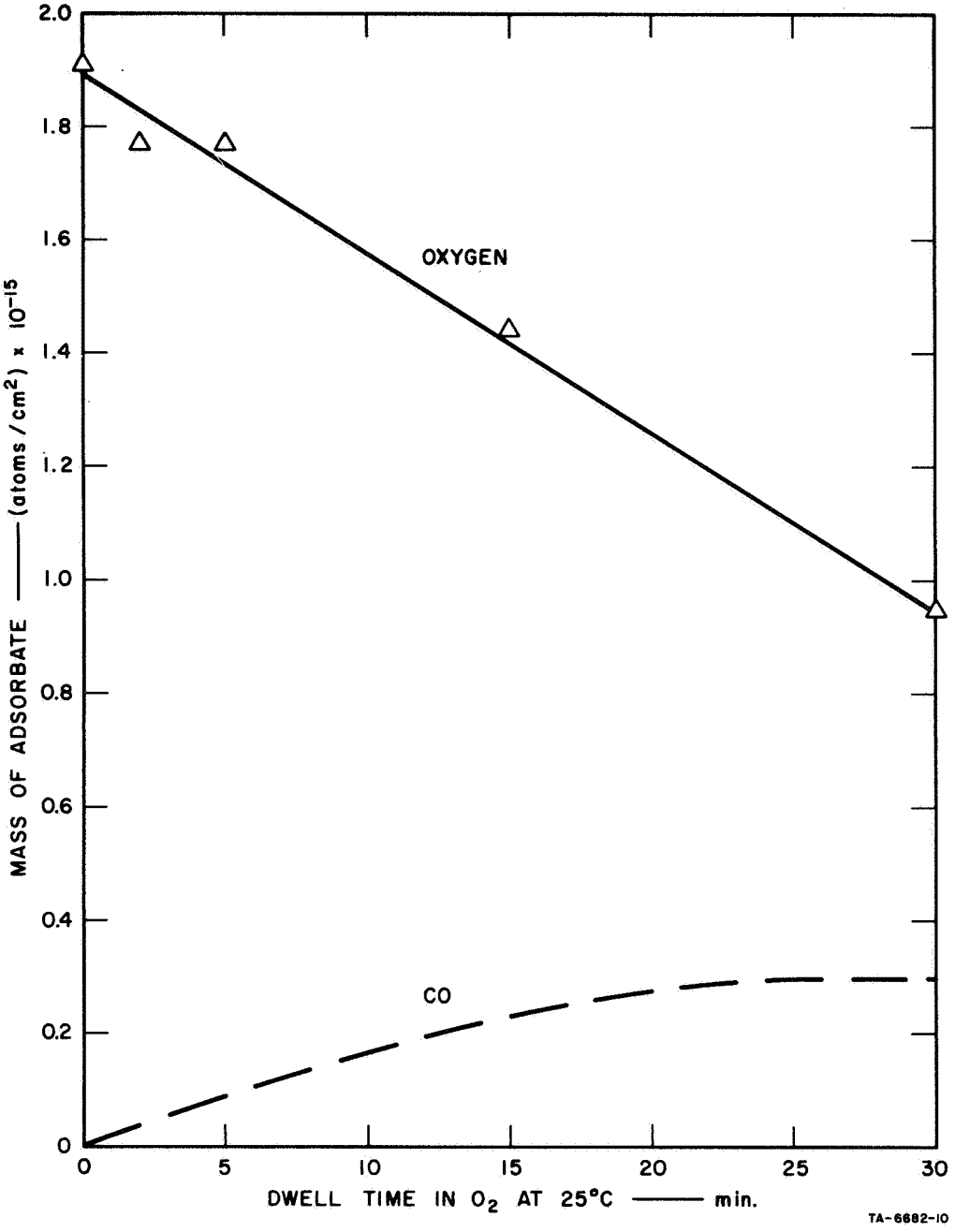

FIG. 4 RATE OF SPONTANEOUS DESORPTION OF OXYGEN FROM GOLD AT 25°C. P_{O_2} = 3 x 10^{-6} torr; at time t = 0, gold surface saturated with sorbed oxygen. Dashed curve: CO sorbed; cf. Fig. 5.

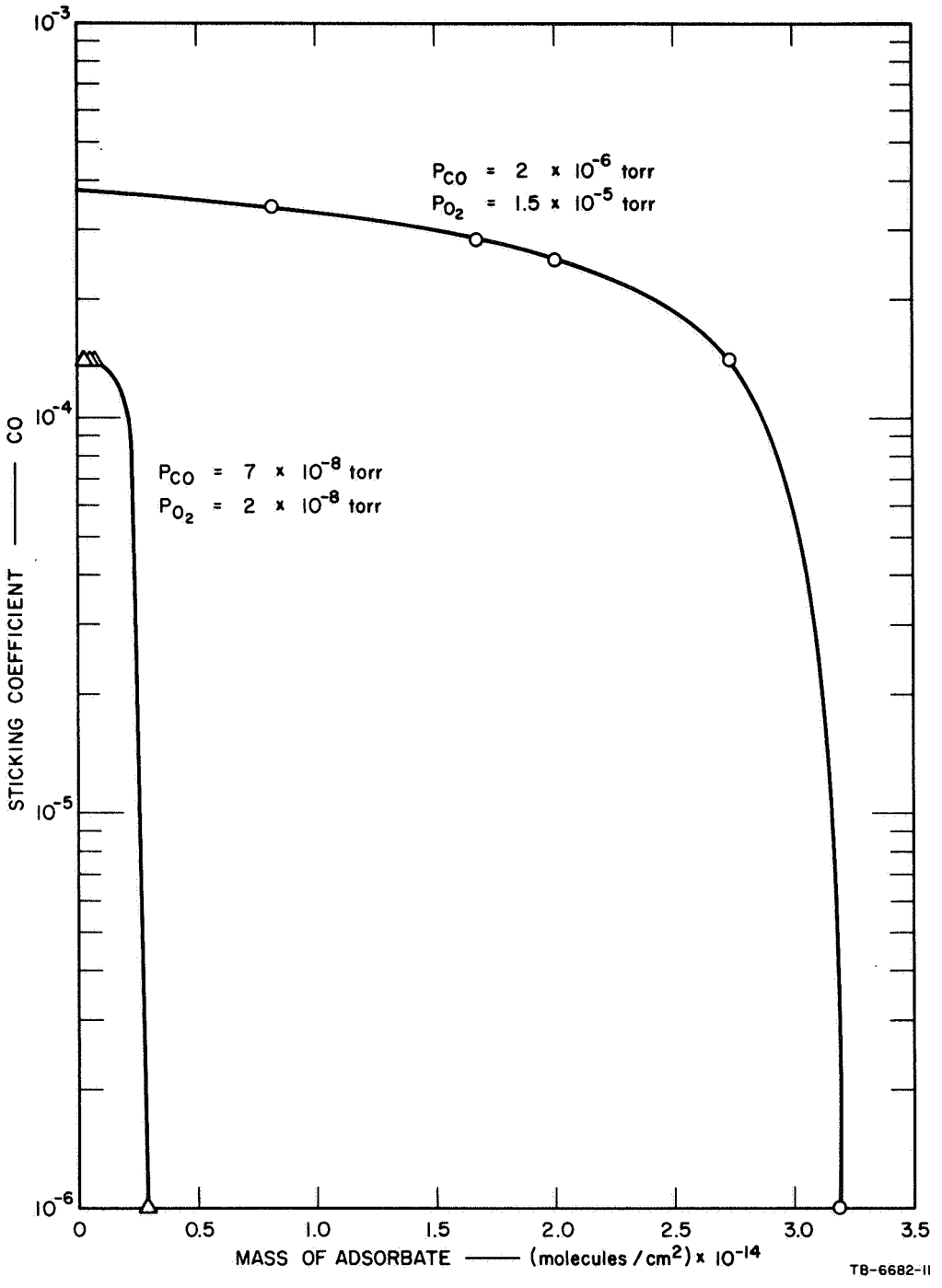

FIG. 5 STICKING COEFFICIENT OF CARBON MONOXIDE ON GOLD IN THE PRESENCE OF MOLECULAR OXYGEN AS A FUNCTION OF CARBON MONOXIDE COVERAGE. T_{gold} = 25°C.